CATALYTIC SOX ABATEMENT OF FCC FLUE GASES

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ABSTRACT

A cerium containing magnesium aluminate spinel catalyst is used as a SOx emission reducing catalyst in the hydrocarbon cracking catalyst regeneration zone. In the regeneration zone this catalyst oxidizes the SO_2 to SO_3 and chemisorbs it as sulfate and releases it as H_2S when it enters the reactor zone. All FCC units are equipped to handle the H_2S that comes out of the reactor. This paper will discuss some of the materials, such as the cerium containing spinels, that were examined as potential SOx catalysts for FCC units and how they were tested for their ability to remove SOx under conditions prevalent in modern FCC units.

INTRODUCTION

Sulfur oxide emissions (SOx = SO_2 + SO_3) from fluid catalytic cracking units (FCCU) are increasingly becoming the target of EPA and local regulations (2). The removal of such pollutants from FCC units has been the subject of a considerable amount of attention over the past few years. The amount of SOx emitted from a FCC unit regenerator is a function of the quantity of sulfur in the feed, coke yield, and conversion. Generally, 45% to 55% of feed sulfur is converted to H_2S in the FCC reactor, 35% to 45% remains in the liquid products, and about 5 – 10% is deposited on the catalyst in the coke (3). It is this sulfur in the coke which is oxidized to SO_2 (90%) and SO_3 (10%) in the FCC regenerator.

$$S \text{ (in coke)} + O_2 \rightarrow SO_2 + SO_3 \qquad 1)$$
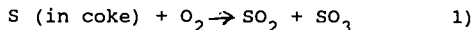
Flue gas scrubbing and feedstock hydrodesulfurization are effective means of SOx control but are laborious and cost intensive. The least costly alternative is the use of a SOx reduction catalyst as an additive to the FCCU catalyst inventory. Designing a catalyst for removal of SOx in a fluid catalyst cracking unit is a challenging problem. One must come up with a particle that will: 1) oxidize SO_2 to SO_3, 2) chemisorb the SO_3, and 3) be able to release it as H_2S as it enters the reactor side of the unit. Another obstacle is the fact that most metals that are in the chemists' repertoire for oxidation or reduction reactions are poisons in the catalytic cracking regime. This paper will discuss some

of the materials that were examined as potential SOx catalysts to remove SOx under conditions prevalent in FCC units.

EXPERIMENTAL

Pseudo boehmite alumina (Condea Chemie), high surface area magnesium oxide (C.E. Basic) and $Ce(NO_3)_3 \cdot 6H_2O$ (Molycorp) were used as received.

Preparation of CeO_2/Al_2O_3: A pseudo boehmite alumina (87.7 g) was impregnated with a solution containing 42.9 g of 70% $Ce(NO_3)_3 \cdot 6H_2O$ (CeO_2 content 28.7%) and 40 g water. This material was dried at $120^{\circ}C$ for 3h and calcined at $700^{\circ}C$ for 1h. Surface area of the catalyst was measured to be 180 m^2/g.

Preparation of CeO_2/MgO: A high surface area Magnesium oxide (87.7 g) was impregnated with a solution containing 42.9 g of 70% $Ce(NO_3)_3 \cdot 6H_2O$ (CeO_2 content 28.7%) and 35 g water. This material was dried at $120^{\circ}F$ for 3h and calcined at $700^{\circ}C$ for 1h. Surface area of the catalyst was measured to be 75 m^2/g.

Preparation of $CeO_2/Mg_2Al_2O_5$: A solid solution spinel $Mg_2Al_2O_5$ was prepared by using required amounts of $Mg(NO_3)_2$ and $NaAlO_2$ as per literature procedure (4-6). A portion (87.7 g) of this material was impregnated with a solution containing 42.9 g of 70% $Ce(NO_3)_3 \cdot 6H_2O$ (CeO_2 content 28.7%) and 40 g water. This material was dried at $120^{\circ}C$ for 3h and calcined at $700^{\circ}C$ for 1h. The surface area of the catalyst was measured to be 140 m^2/g.

Thermal studies: Thermogravimetric studies were used for the testing of the materials. This was accomplished by placing a small amount (5 - 25 mg) of virgin sample on a quartz pan and passing a desired gas. The experiment was divided into four zones:

Zone A: Under N_2, the sample was slowly (20°C/min.) heated to 700°C. This takes about 35 min.

Zone B: Nitrogen was replaced by a gas containing 0.32% SO_2, 2.0% O_2, and balance N_2. The flow rate was 200 mL/min. The temperature was kept constant at 700°C. This condition was maintained for 30 min.

Zone C: Passage of SO_2 containing gas was ceased and replaced by N_2. Temperature was reduced to 650°C. This is a 15 min. time zone.

Zone D. Nitrogen was replaced by pure H_2. This condition was maintained for 20 min.

Fluidized bed test: A one inch diameter quartz reactor heated by a tube furnace was connected to a gas manifold. Reactor temperature was controlled by a temperature controller with a thermocouple in the middle of the fluidized catalyst bed. A schematic diagram is shown in Figure 5. A blend of DeSOx catalyst in equilibrium FCC catalyst was made such that the concentration of DeSOx catalyst was 1.5 weight per cent.

15 grams of this blend was charged into a quartz reactor. The blend was cycled as described below.

   SOx Pickup Side of Cycle

a. The blend was heated to $732^\circ C$ in flowing N_2.
b. At $732^\circ C$ N_2 was discontinued, and 5.9% O_2 was allowed to pass through the bed for 4 minutes.
c. Then 1.5% SO_2 was introduced along with the air for a 15 minute period at $732^\circ C$. Approximately 105-115 mg SO_2 was delivered during the test. The reactor effluent was trapped in a peroxide trap.
d. After 15 minutes of test with SO_2, the SO_2 flow was stopped, but the oxygen remains on for an additional 4 minutes.
e. Oxygen was replaced with nitrogen for ten minutes at $732^\circ C$.
f. The catalyst bed was cooled under flowing nitrogen for about 30 minutes.
g. The peroxide trap was disconnected and worked up as per EPA test no. 6.

   H_2 Reduction Side of Cycle

a. The blend was flushed with N_2 and brought to a temperature of $732^\circ C$.
b. At $732^\circ C$ the N_2 was shut off, and the catalyst subjected to 100% H_2 for 5 minutes. The reactor effluent was captured in a 1M NaOH trap.
c. The system was flushed with N_2 at $732^\circ C$ for 10 minutes, then cooled under flowing N_2.
d. Sulfur analysis of the trap determined the amount of sulfur removed with each H_2 treatment.

RESULTS AND DISCUSSION:

   The sulfur in the coke is mainly oxidized (7) to SO_2 (equation 1). Sulfur dioxide should be further oxidized to SO_3 (equation 2) so that it can be reactive (8) towards metal oxides to form sulfate (equation 3).

$$2SO_2 \ + \ O_2 \ = \ 2SO_3 \qquad\qquad 2)$$

$$SO_3 \ + \ MO \ = \ MSO_4 \qquad\qquad 3)$$
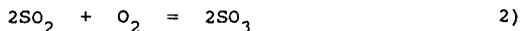
As the operational temperature of the regenerator is increased the formation of SO_3 is less favored (7). The free energy of formation of SO_3 (equation 2) is -9.5 KJ/g-mole at 675 C and -4.4 KJ/g-mole at 730°C. The regenerator temperature of an FCC unit is between 650 to 775°C. Catalyzing reaction 2 is one of the major functions of a SOx catalyst. Equation 3 represents the capture of SO_3 in the regenerator by the catalyst. The catalyst then moves to the FCCU reactor where the sulfate is reduced by hydrogen and other reducing gases to metal oxide and H_2S (equation 4) or metal sulfide (equation 5).

$$MSO_4 + 4H_2 = MO + H_2S + 3H_2O \qquad 4)$$

$$MSO_4 + 4H_2 = MS + 4H_2O \qquad 5)$$
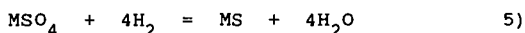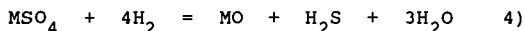
Metal sulfide can be hydrolyzed in the stripper to form the original metal oxide (equation 6).

$$MS + H_2O = MO + H_2S \qquad 6)$$
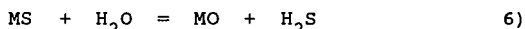
This generally accepted mechanism (3,9-12) and a schematic diagram of an FCCU is shown in Figure 1. A SOx reduction catalyst, thus, has three functions: oxidation, chemisorption, and reductive decomposition. Vanadium pentoxide (13) is an excellent oxidation catalyst and is specially useful for the oxidation of SO_2 to SO_3. However, V_2O_5 cannot be used in an FCC unit because it reacts with zeolites present in an FCC catalyst. Our laboratory experiments indicate that platinum can be used for this purpose (4), but it is expensive and is not very effective under actual FCC regenerator conditions (14). Iron oxides are also very effective oxidation catalysts but iron enhances the formation of coke and unfavorably changes the product distribution. Our tests with iron containing catalysts clearly indicate that more coke is formed causing more than normal SO_2 generation in the regenerator. Cerium dioxide can be used for the oxidation of SO_2. We have found that under FCC conditions CeO_2 is an excellent oxidation catalyst (equation 7) and it regenerates quickly under oxygen (equation 8). An FCC regenerator contains 1 to 3% oxygen.

$$2CeO_2 + SO_2 = SO_3 + Ce_2O_3 \qquad 7)$$

$$Ce_2O_3 + 1/2O_2 = 2CeO_2 \qquad 8)$$
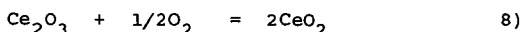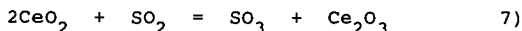
Once the SO_3 is formed, it has to be chemisorbed by the catalyst. Alumina can be used for this purpose to form $Al_2(SO_4)_3$ (equation 9).

$$Al_2O_3 + 3SO_3 = Al_2(SO_4)_3 \qquad 9)$$
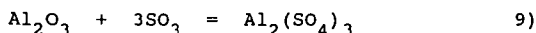
One of the catalysts that was tested by us and others (15) is CeO_2 on gamma alumina. This can be conveniently prepared by impregnating gamma alumina with $Ce(NO_3)_3 \cdot 6H_2O$ solution followed by drying and calcining at $730^{O}C$ for 3h. The amount of CeO_2 was 12.3%. Aluminum sulfate starts to decompose at $580^{O}C$ (16). Hence one disadvantage of using this catalyst is the fact that any FCC regenerator operating at a temperature higher than $600^{O}C$ should have some decomposition of $Al_2(SO_4)_3$ (backward reaction of equation 9). A thermogravimetric analysis (TGA) of this catalyst is reported in Figure 2. The catalyst was first preheated to $700^{O}C$ under N_2 (zone A). Then it was exposed to a gas containing 0.32% of SO_2, 2.0 % O_2 and balance N_2 at a flow rate of 200 mL/min.(zone B). The weight gain of 5.5% indicated in figure 2 is the amount of SO_3 formed (reaction 7) and absorbed (reaction 9) to form the $Al_2(SO_4)_3$. The TGA indicates that only 2.5% of all the available Al_2O_3 is involved in picking up SO_3 during the first 15 min. period. This number is called SO_2 oxidation and absorption index (SOAI)(17). The SOAI of 2.5 for this catalyst is very low when compared to other catalysts described in this paper. The activity decreases considerably during the second 15 min. period. Zone C is when the passage of SO_2 containing gas was ceased and replaced by pure N_2. At this point the temperature was dropped to $650^{O}C$ to mimic the FCC conditions. TGA clearly shows that at this temperature the $Al_2(SO_4)_3$ is thermally unstable and releases some of the SO_3 it absorbed in zone 2. However, once the sulfate is formed alumina is regenerated under H_2 fairly easily because aluminum sulfate reduces at 400 to $700^{O}C$, which is in the FCC reactor temperature range (equation 10). Figure 2, zone D, is indicative of an efficient reduction of $Al_2(SO_4)_3$ to Al_2O_3 (equation 10). Alumina is regenerated in about 2 min.

$$Al_2(SO_4)_3 \ + 12H_2 \ = \ Al_2O_3 \ + 3H_2S \ + 9H_2O \qquad 10)$$
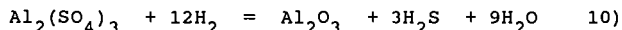
The low SOAI and the thermal instability of the sulfate under FCC conditions clearly indicate that CeO_2 in gamma alumina is not a very effective DeSOx catalyst.

A catalyst was prepared by impregnating MgO with cerium nitrate solution. The composition of the final calcined catalyst was 12.3% CeO_2 on MgO. Since MgO is much more basic than Al_2O_3 it was hoped that it would be more reactive towards SO_3. A TGA analysis is shown in Figure 3. The catalyst gains 28.5% weight in 30 min. due to SO_3 absorption (zone B). This is 5.2 times more than the CeO_2/Al_2O_3 catalyst. The SOAI of this catalyst is 8.7 which indicates that the SO_3 absorptivity of CeO_2/MgO catalyst is 3.5 times higher than the corresponding alumina catalyst during the first 15 min. Linearity of the absorption plot (zone B) indicates that the absorption during the second 15 min. is as efficient as the first 15 min. When the passage of the SO_2 containing

gas was ceased and replaced by dry N_2 (zone C), unlike CeO_2/Al_2O_3 cata-
lyst, this material did not lose any weight indicating the thermal sta-
bility of the $MgSO_4$. Magnesium sulfate is not expected to decompose
below $780^{\circ}C$ (16). Under H_2, the sulfate formed reduces at $650^{\circ}C$ (zone
D), however, the MgO can not be regenerated as efficiently as the
alumina catalyst. About 7.7% of the absorbed material still remains
with the catalyst even after 20 min. of H_2 reduction, possibly as MgS or
unreduced $MgSO_4$. Fast deactivation of this catalyst is one of the major
reasons why CeO_2/MgO was not considered as a potential DeSOx catalyst
for FCC units.

The higher reactivity of MgO prompted us to look for a compound
that was more thermally stable. Magnesium aluminate spinels such as
$MgAl_2O_4$ or $Mg_2Al_2O_5$ were the ones we selected. The latter is a solid
solution of pure spinel ($MgAl_2O_4$) and MgO. Such a solid solution does
not destroy the spinel framework. These spinels can be prepared by the
calcination of Mg,Al double hydroxides, formed by the reaction of
$Mg(NO_3)_2$ and $NaAlO_2$ at pH 8.5 to 9.5. (4-6). The spinel structure is
based on a cubic close packed array of oxide ions. Typically, the crys-
tallographic unit cell contains 32 oxygen atoms; one eighth of the
tetrahedral holes (of which there are two per anion) are occupied by the
divalent metal ion (Mg^{2+}), and one-half of the octahedral holes (of
which there is one per anion) are occupied by the trivalent metal ion
(Al^{3+}).

A catalyst prepared by the impregnation of $Mg_2Al_2O_5$ with $Ce(NO_3)_3$
was tested for SOx removal activity. The final composition was 12.3%
CeO_2 on $Mg_2Al_2O_5$. A TGA analysis of this material is reported in Figure
4. During preheating (zone A) the material desorbed 7.6% moisture.
This material gains 23.3% weight by the absorption of SO_3 which is about
the same as the CeO_2/MgO catalyst. The SOAI of this material is 17
indicating that this catalyst is 6.8 times more active than the
CeO_2/Al_2O_3 catalyst. We have previously seen that SO_3 absorption by
alumina is negligible and MgO is an extremely efficient SO_3 absorbing
agent. This indicates that in a spinel it is the MgO structural
fragment that is reacting with the SO_3 and our SOAI calculations for
spinel catalysts are based on this concept. The SOAI of the spinel
containing catalyst is about twice that of the CeO_2/MgO catalyst. This
indicates that the absorption activity of MgO in spinel is much higher
than that of pure MgO, possibly due to the dispersion of MgO in the
spinel. Linearity of the absorption plot (zone B) indicates that the
absorption in the second 15 min. period is as efficient as the first 15
min. period. When the passage of SO_2 containing gas was ceased and
replaced by pure N_2 (zone C) no weight loss was observed. This indi-
cates that in zone B only $MgSO_4$ is formed although this catalyst has
nearly 50% alumina. Unlike the CeO_2/MgO catalyst this catalyst regener-
ates efficiently under H_2 (zone D). The catalyst completely regenerates

in twenty minutes of H_2 reduction. Although this reduction time is much longer than that experienced in an actual FCC unit, it can be used to compare potential catalysts. It is clear, if we compare Figures 3 and 4, that $MgSO_4$ reduces much more efficiently in a spinel catalyst compared to pure MgO. This may be due to the fact that MgO in a spinel matrix is more sterically hindered than in a magnesia unit cell. Therefore, any sulfate formed whose decomposition would relieve the steric strain is favored, i.e. the decomposition of a sulfated spinel is thermodynamically more favorable than the decomposition of a sulfated magnesia sample.

Since we realized that a cerium containing magnesium aluminate spinel is the most efficient DeSOx catalyst that we have tested, a laboratory scale fixed fluidized bed reactor system was set-up (figure 5). Absorption and reduction half-cycles are repeated as described in figure 6 to mimic FCC units. Our system used a one inch diameter quartz reactor that was connected to a gas manifold so that the catalyst could be subjected to different gas mixtures. Reactor temperature was controlled by a controller with a thermocouple in the middle of the fluidized catalyst bed. In most cases a blend of DeSOx catalyst in equilibrium catalyst was made, then subjected to a $760^\circ C$, 6 hour steaming treatment, and finally tested for SOx pickup. The gas stream was analyzed by absorbing the exit gas in a H_2O_2 trap over a period of time, and then using the EPA 6 method for determining SO_2. The gas stream could also be analyzed instantaneously by an IR analyzer as long as care was taken to remove any SO_3 from the gas stream. In most cases, the sulfated sample was subjected to a reduction with either hydrogen or propane and followed by another SOx pickup. This cycle could be repeated several times to see the effect of adding and removing sulfur to a potential DeSOX catalyst. By adding solenoid controls to the gas lines and a microprocessor the whole system was eventually computerized so that constant monitoring by an individual was not necessary and runs could be made overnight.

Results obtained from fluidized bed tests are reported in Tables 1 and 2. Tables 1 and 2 represent the results obtained from virgin catalyst and a steam deactivated ($760^\circ C$, 6h, 100% steam) catalyst, respectively. The amount of sulfur picked up was calculated by difference between the amount delivered and the amount found in the trap. The amount of sulfur removed was determined by gravimetric analysis of the contents of the NaOH traps. The concentration of DeSOx catalyst was 1.5 wt% in FCC catalyst. The Tables 1 and 2 indicate that steaming only causes a very minor deactivation. Nearly 90% of the fresh activity is retained even after steaming. Moreover, this catalyst picks up sulfur nearly half of its theoretical maximum in 15 min. indicating very high

activity. A mechanism of SOx reduction showing the catalytic cycle is illustrated in Figure 7. This cycle is given to describe the catalytic nature of the DeSOx components. In the figure, the catalyst $CeO_2/Mg_2Al_2O_5$ is represented by its active cites, namely CeO$_2$ and MgO.

CONCLUSION

A cerium containing magnesium aluminate spinel material was found to be the most effective DeSOx catalyst that we have studied. This spinel based catalyst was commercialized and is recognized as the leading DeSOx catalyst for FCC units.

ACKNOWLEDGEMENTS

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17. SOAI = SO_2 Oxidation and Absorption Index; defined as the percentage of absorbent that is involved in picking up SO_3 which is produced by the oxidation of SO_2 in presence of the catalyst in 15 min. at a standard TGA condition

Table 1

Sulfur Picked Up And Removed at 732°C
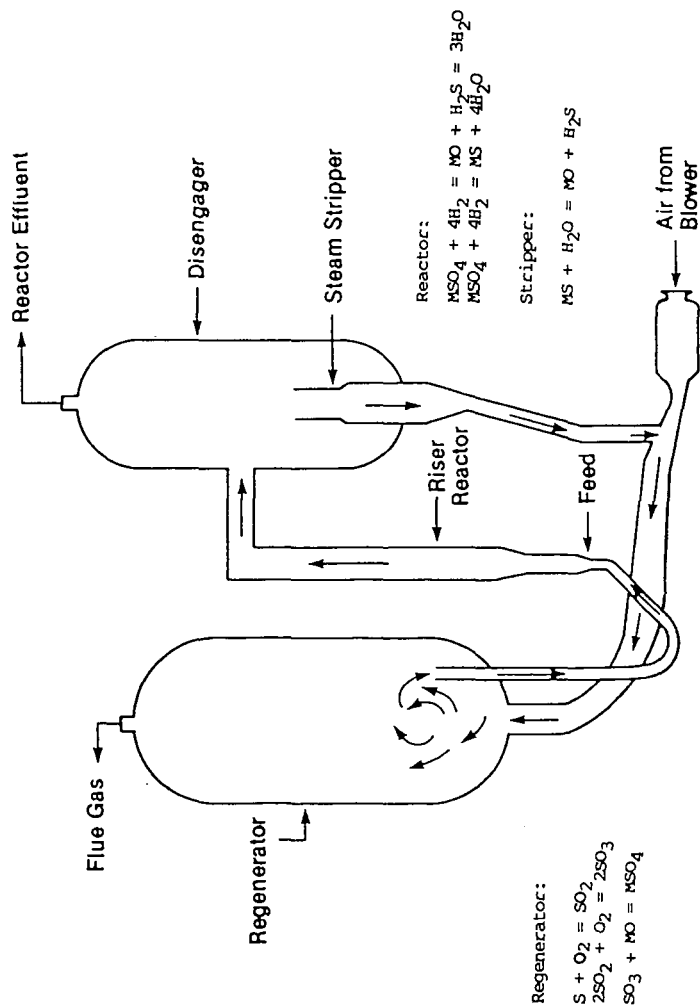On Virgin 12.3% CeO_2 On $Mg_2Al_2O_5$

SOx Pickup-H_2-Reduction	Mg Sulfur Theoritical Maximum	Mg Sulfur Picked Up	Mg Sulfur Removed
First Cycle	79	44	45
Second Cycle		42	44
Third Cycle		39	39
Fourth Cycle		37	37
Fifth Cycle		38	40
Sixth Cycle		37	-

Table 2

Sulfur Picked Up And Removed At 732°C
On Steamed 12.3% CeO_2 On $Mg_2Al_2O_5$

SOx Pickup-H_2-Reduction	Mg Sulfur Theoritical Maximum	Mg Sulfur Picked Up	Mg Sulfur Removed
First Cycle	79	39	38
Second Cycle		36	36
Third Cycle		34	35
Fourth Cycle		31	35
Fifth Cycle		28	-

FIGURE 1

SCHEMATIC DIAGRAM OF A TYPICAL FCC UNIT

Reactor Effluent

Disengager

Steam Stripper

Reactor:

$$MSO_4 + 4H_2 = MO + H_2S = 3H_2O$$
$$MSO_4 + 4H_2 = MS + 4H_2O$$

Stripper:

$$MS + H_2O = MO + H_2S$$

Air from Blower

Riser Reactor

Feed

Flue Gas

Regenerator

Regenerator:
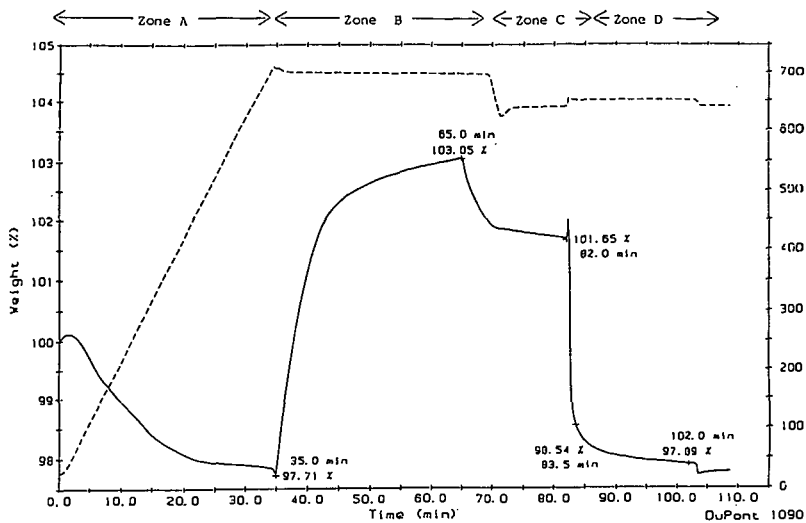
$$S + O_2 = SO_2$$
$$2SO_2 + O_2 = 2SO_3$$
$$SO_3 + MO = MSO_4$$
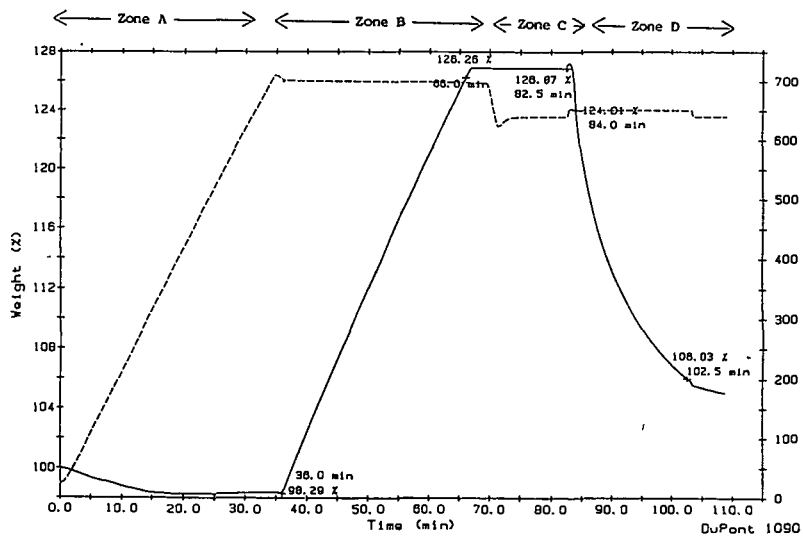
407

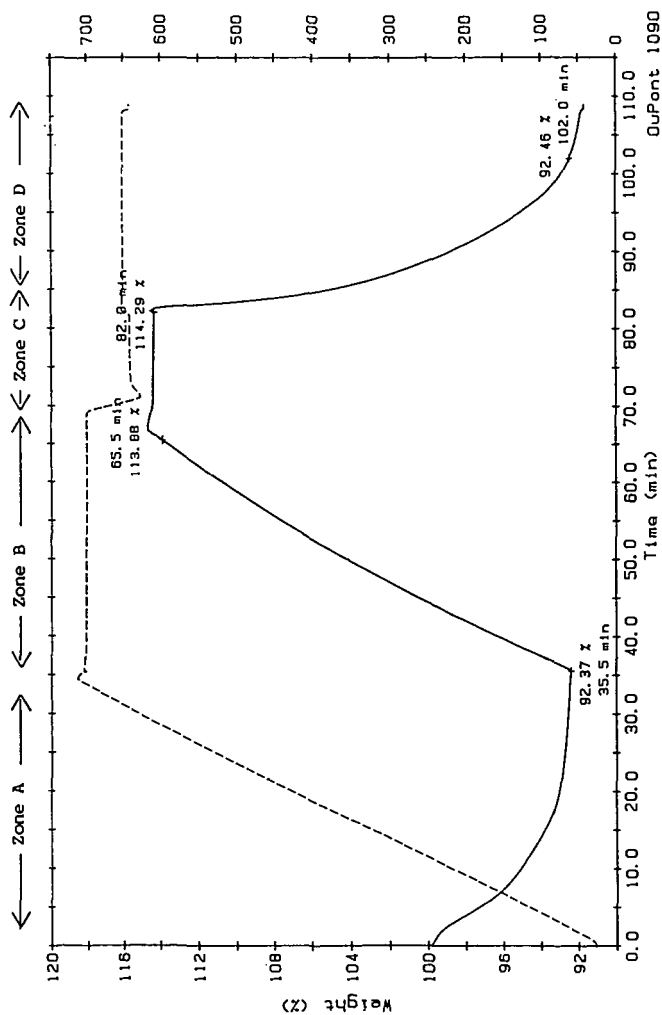Figure 2. TGA Test of a CeO$_2$/Al$_2$O$_3$ Catalyst

Figure 3. TGA Test of a CeO$_2$/MgO Catalyst

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Figure 4. TGA Test of a $CeO_2/Mg_2Al_2O_5$ Catalyst

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Figure 5

A Laboratory Scale Fixed Fluidized Bed Reactor System

Impinger

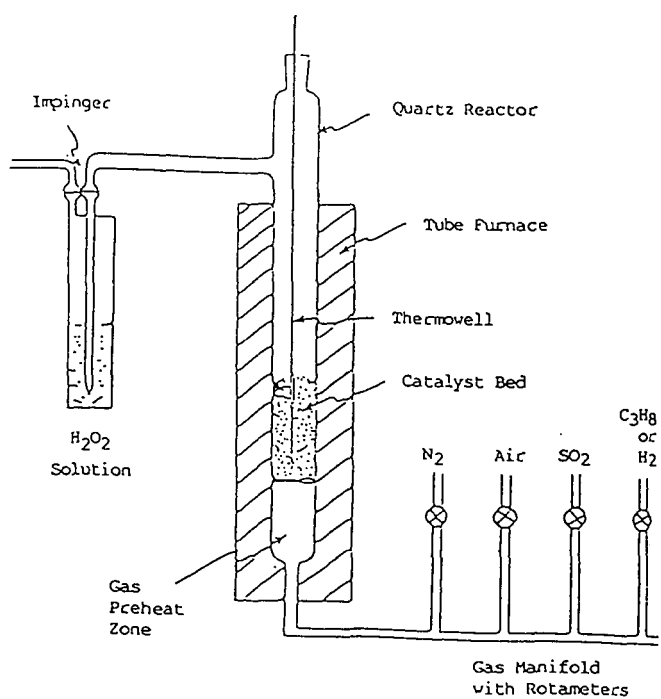Quartz Reactor

Tube Furnace

Thermowell

Catalyst Bed

H_2O_2
Solution

N_2 Air SO_2 C_3H_8
                          or
                          H_2

Gas
Preheat
Zone

Gas Manifold
with Rotameters

Figure 6

Adsorption And Reduction Half Cycle

N₂ Purge

SOx Pickup

1.5% SO₂ + 5.0% O₂
@ 1350°F for 15 min

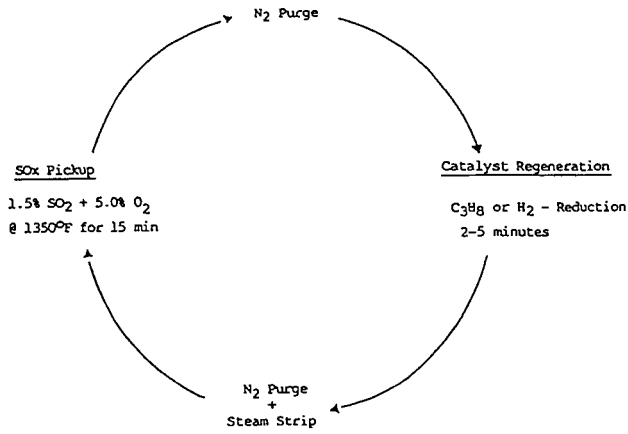Catalyst Regeneration

C₃H₈ or H₂ – Reduction
2-5 minutes

N₂ Purge
+
Steam Strip

Figure 7

DeSOx Mechanistic Cycle

$MgO \equiv CeO_2$

H_2S

H_2

SO_2

$MgSO_4$

Ce_2O_3

SO_3

O_2

$MgO \equiv CeO_2$

$CeO_2/Mg_2Al_2O_5 \equiv MgO \equiv CeO_2$

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